CO hydrogenation with Co catalyst supported on porous media

K. Sapag [a,*], S. Rojas [b], M. López Granados [b], J.L.G. Fierro [b], S. Mendioroz [b]

[a] *Laboratorio de Ciencias de Superficies y Medios Porosos, Dpto de Física,
Universidad Nacional de San Luis, 5700 San Luis, Argentina*
[b] *Instituto de Catálisis y Petroleoquímica, CSIC, Campus UAM, 28049 Madrid, Spain*

Abstract

In this work, pillared clays as Co catalysts supports were studied in the CO hydrogenation called Fischer–Tropsch (FT) reaction.

Two supports were prepared by different methods [K. Sapag, Ph.D. Thesis, Universidad Autónoma de Madrid, 1997, Madrid, Spain] with the same metal/clay ratio. They were impregnated with 20% of cobalt in salt solution and calcinated to obtain the catalysts. The reaction was realised at 20 bar of pressure and temperatures between 200 and 280°C approximately.

The results show a better selectivity to products with certain carbon chain size for one of the supports, due probably to its textural properties. This selectivity was investigated through a series of additional experiences in which different catalysts were prepared and probed, among them a FT standard catalyst.

The catalyst that shows the best results not only has good shape selectivity, besides, it also has better intrinsic activity if compared with the FT standard catalyst. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pillared clays; Fischer–Tropsch; Syngas reaction; Co catalyst; Shape selectivity

1. Introduction

Catalytic synthesis made from syngas (CO and H_2) yield a great variety of products [2]: paraffins, olefins, alcohols, etc. depending on the catalysts used and on the process conditions. The process, denominated Fischer–Tropsch synthesis (FTS), is utilised at industrial scale in Malaysia and South Africa [3] where it is profitable. The reaction mechanism accepted [4] consists of a polymerisation that leads to a distribution of products with different molecular weight, called Anderson–Schulz–Flory distribution (ASF). This distribution determines a lineal relationship between the logarithm of the product yield versus the number of carbons [5], showing a lack in the selectivity and obtaining hydrocarbons from gases to waxes [6]. Some metals show activity in FTS [7], being the Co the active metal with the widest distribution in the carbon chain products.

The production of gasoline and diesel by hydrogenation of CO is an interesting alternative to the use of petroleum [8]. To optimise the production of liquid hydrocarbons in FT synthesis is necessary to modify the ASF distribution. One way to make this modification is by reducing the production of heavy hydrocarbons trough geometric impediments in the catalysts avoiding the chain carbon growth, if we accept that the mechanism of this reaction is a polymerisation process.

Pillared clays (PILCs) are bi-dimensional porous materials [9] with an adequate porous texture to be

---

* Corresponding author.
E-mail address: sapag@unsl.edu.ar (K. Sapag).

used in FT reaction. Utilising these materials as support, a limitation in the growth of the products would be reached, due to its specific porous size.

Since aluminium pillared clays (Al-PILCs) have demonstrated a high selectivity to the adsorption of normal paraffins in the range C_6–C_{10} [10] and Co is known as a good FT metallic catalysts, in the present work, Co catalysts supported on two kinds of Al-PILC were prepared and probed in the FT reaction obtaining important results.

2. Experimental

2.1. Methods and techniques

The analysis of the previously disintegrated sample was made by atomic absorption spectrophotometry (AAS) with equipment Perkin-Elmer® model 3030.

The study of the changes in the structural and mineral composition was made with the X-ray diffraction (XRD) technique called "dust method" with a diffractometer SEIFERT®-XRD 3000 with Cu anode and Ni filter. The diffractograms were obtained from θ:2θ with steps of $0.02°$ and a retention time of 1 s in each angle.

To analyse the texture of the samples the BET-method was used. Nitrogen isotherms were obtained with a nitrogen sorptometer Micromeritics® ASAP-2000. The microporous region data were calculated with the equation of Harkins and Jura, and the total pore volume according to the Gursvitch rule (applied at $p/p^0 = 0.98$). The samples (0.3–0.8 g) were previously degassed at $300°C$ during 18 h approximately and then studied at $-196°C$. The TPR analysis was made with a Micromeritics equipment, TPD/TPR 2900 with a gas flow of $90 \, cm^3 \, min^{-1}$ of Ar and $10 \, cm^3 \, min^{-1}$ of H_2.

The catalytic reaction was held in a stainless steel fixed bed, at 20 bars of pressure with a relationship $H_2/CO = 2$ and GHSV $= 6120 \, h^{-1}$. The sample weighting 0.35 g with a particle size between 0.25–0.4 mm was used in each experiment. The products were analysed on line in a chromatographic system with three columns: a Haye Sep column on series with a packed column and then on parallel with a capillary column; and two detectors FID and

TCD. The heavy hydrocarbons were collected on a condensing system after the analysis. The conversion data were calculated from the conversion of CO.

2.2. Synthesis of the support

A natural clay with a high percentage of montmorillonite (90.67%), quartz (4.14%) and feldspar (5.19%) from Serrata de Nijar, Almeria, Spain, called SerBca was used as the former material. After a purification process, by Stokes method, the clay denominated SerBcaP remains free of quartz. A latter material was obtained with the following characteristics: $0.79 \, meq \, g^{-1}$ of cationic exchange capacity (CEC); $12.6 \, \text{Å}$ of basal distance calculated by XRD; $72 \, m^2 \, g^{-1}$ of BET specific area and an approximate structural formulae determined by AAS:

$$(Al_{2.880} + Fe_{0.423} + Mg_{0.705} + Mn_{0.003})_{VI}$$
$$+ (Al_{0.097}) + Si_{7.903})_{IV} O_{20}(OH)_4 M_{0.77}$$
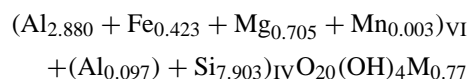
where VI and IV are refereed to the co-ordination number in the octahedral and tetrahedral position, respectively, and M corresponds to the interchange cations.

Two methods were used in the preparation of PILCs [1]:

1. *Conventional method.* The pillaring oligocation was prepared from 0.2 M of $AlCl_3 \cdot 6H_2O$ solution and 0.5 M of NaOH solution, with a basicity relationship OH/Al $= 2$. The sodium hydroxide solution was incorporated drop by drop into the aluminium chloride solution, which was maintained under stirring at $60°C$. The resultant solution was aged under reflux conditions during 48 h. The polymeric solution was incorporated drop by drop into a suspension made with 5% of clay purified and homo-ionised with Na (denominated SerBcaNa) into de-ionised water. The amount of the incorporated oligocation had a ratio of 20 meq of Al per gram of clay. The sample was washed in a dialysis membrane, dried at $60°C$ and calcinated at $500°C$ for 2 h. The resulting material was denominated Al500.

2. *Quick method.* The oligocation of Al was prepared with a solution from the commercial product Locron® (aluminium chlorhydrate) which

was incorporated drop by drop into a suspension made with 50% of natural clay (SerBca) into a mixture of water and acetone. The basicity ratio was 2 and the quantity of Al was 20 meq per gram of clay. Then, the material was washed, dried and calcinated in the same way as described in the previous method. This resulting material was denominated Loc500.

2.3. Preparation of catalysts

Co catalysts were prepared by impregnation with a $CoNO_3$ solution of the PILCs as supports. The Co content was 20% in weight and the catalysts were labelled as Co20Al and Co20Loc for Al500 and Loc500 as supports, respectively.

3. Results and discussion

3.1. Characterisation

In Fig. 1 the XRD spectra are shown. Note that the incorporation of Co to Al500 has a reduction in the basal space of the support accompanied by a decrease

on the intensity of the corresponding peak. The same occurs with the catalyst supported on Loc500 where this effect is higher. In both catalysts appear weak peaks of Co oxides (Co_3O_4, Co_2O_3, CoO) [11–13] with distances at 2.85; 2.43; 2; 1.6; and 1.43 Å.

In Fig. 2 the adsorption–desorption isotherms from the catalysts and from the supports are shown. The incorporation of the active phase modifies the texture of the PILCs. In both catalysts a diminution of the volume adsorbed in the microporous zone is observed, if compared with the supports. The mesoporous zone is lightly affected by Co as is observed in the parallelism of the isotherm adsorption branches. Nevertheless, a diminution in the hysteresis loop is observed, probably due to the excess of Co in the union between the layers. The effect of the incorporation of the active phase in the textural properties is higher in Co20Loc than in Co20Al, at identical concentrations.

In Table 1, the most important characteristics of the samples obtained by XRD and N_2 adsorption–desorption are reported, where it is notorious the influence of the impregnation over the porous structure of the support. In this table, we note that the addition of Co to Al500 support decreases its microporosity in almost 30%. On the sample supported over Loc500
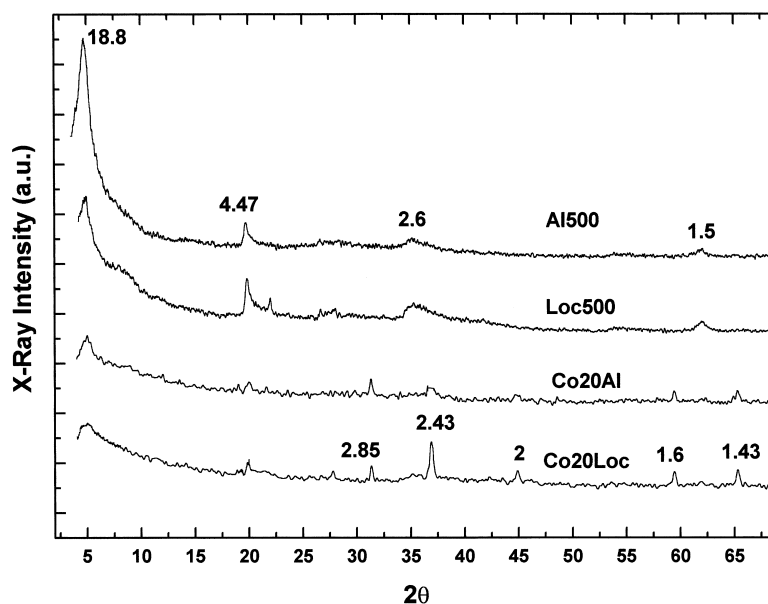

Fig. 1. XRD patterns of both PILCs and prepared catalysts. The characteristic peaks in Al500, corresponding to the montmorillonite and the basal distance of PILC, as well as the peaks of cobalt oxides that appear in Co20Loc are remarked.
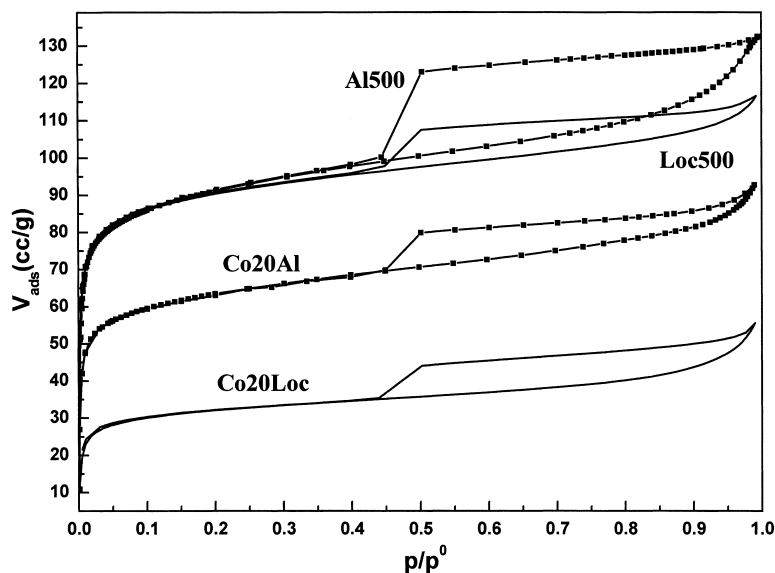
Fig. 2. N_2-isotherms of both PILCs and prepared catalysts. The nitrogen adsorbed volume (in cm^3) per gram of sample vs. relative pressure of nitrogen is shown.

the decrease in the microporosity is about 70%. The higher effect of Co in the Co20Loc support is shown by the low surface area of the sample. Since the Co concentration and the preparation conditions are the same in both samples, it could indicate the presence of different pillaring cation in each PILC.

To conclude, Al500 is less affected after the impregnation process, especially in the porous range under study (10–50 Å).

Due to the fact that in FTS the active phase is Co in metallic form, TPR studies were realised. In Fig. 3 the curves of Co catalysts obtained by TPR are shown. From the calculations made with these data we conclude that the stoichiometry reduction [14,15] is not accomplished in any of the samples, supposing that

the initial state of Co is Co_2O_3. As a consequence, a mixture of Co oxides appears in the samples as it is shown in XRD diffractograms. In Co20Al only a small fraction of the Co could appear as Co_2O_3 extralayered; the rest could keep forming CoO intralayered, less oxidised probably due to diffusional problems. In Co20Loc the intralayered fraction is much smaller. Additionally, dispersed phases could appear due probably to the Co incorporated to the Al pillars — both on the pillar surface [16] and forming the corresponding spinel [17] — given by the wide peak at about 600°C. In Co20Loc, this last effect is less notorious, as only a very small fraction of Co would be incorporated to the pillar. In both samples, at 600°C the highest amount of cobalt oxides is found in its reduced state.

Table 1
Characterisation data from the prepared catalysts[a]

Sample	d_{001} (Å)	S_{BET} ($m^2 g^{-1}$)	$V_{\mu p}$ (cc g^{-1})	V_{mp} (cc g^{-1})	V_T (p/p$^0 \approx 0.98$) (cc g^{-1}
Al500	18.8	336	0.091	0.067	0.199
Co20Al	17.9	238	0.061	0.045	0.139
Loc500	19	344	0.096	0.050	0.177
Co20Loc	17.5	121	0.030	0.030	0.081

[a] where d_{001} is the basal distance measured by XRD; S_{BET}, $V_{\mu p}$, V_{mp}, V_T are, respectively, the specific area, the micro and mesoporosity and the total porous volume calculated at $p/p^0 \approx 0.98$ from the data of the nitrogen isotherm.
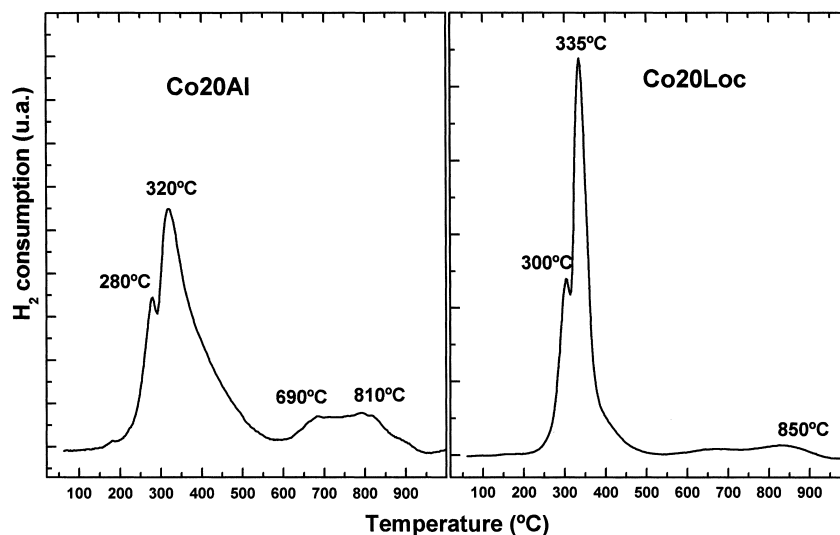
Fig. 3. Thermal-programmed reduction (TPR) of the prepared catalysts.

From the characterisation data we can infer that in Co20Al the Co incorporation is high in the micro and mesoporous range, but the variation in the total porosity is not very important. Then, a part of the active phase is incorporated into the walls of the small porous without blocking them. On the contrary, for Co20Loc, a high amount of Co is in the surface and the porous volume is reduced after the incorporation of the active phase, perhaps, due to the Co is blocking some porous.
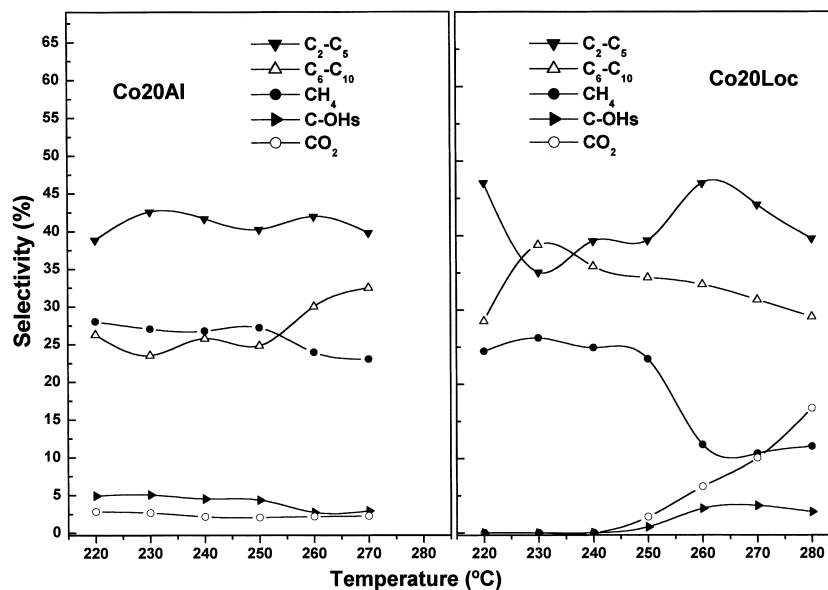
Fig. 4. Selectivity of the products for the hydrogenation of CO with the prepared catalysts vs. temperature in Celsius degree.

3.2. Reaction

Before activity test, the catalysts were reduced in situ at 600°C by 1 h and cooled down in He atmosphere to room temperature. Subsequently, the pressure was turned up until 20 bars and the reacting mixture was introduced. After the stabilisation of the system, the temperature was set up to its initial value of reaction. This reaction is highly exothermic and the analysis of the products is not easy [18].

In Fig. 4, the selectivity of the products is shown, grouped in methane, alcohols, gases and liquids, versus the temperature for the analysis of products up to C_{10}. The distribution of products shows a low formation of CO_2 in the Co20Al catalyst.

In Fig. 5, the CO conversion versus temperature for the samples under study is shown. Despite of the incorporation of the same quantity of the metal in both samples it is observable a higher activity for Co20Al than for Co20Loc. This difference in the behaviour of the catalysts can be attributed to: (1) a worse dispersion of the Co in Loc500 than in Co20Al according to the smaller surface area showed by Co20Loc, which leads to a minor activity and (2) to the different pore size distribution of the support, principally in the microporous range.

In Fig. 6, the selectivity (%) of detected compounds versus the number of carbons is shown, where neither methane nor CO_2 have been taken into account. The selectivity patterns show an important result reported for first time: the distribution of the products obtained with Co20Al faster decreases with the increasing number of carbons. This may be attributed to a limitation in the growth of the carbon chains. To investigate this fact, a Co standard catalyst for FT [19] was synthesised by precipitation with 30% of Co as the active phase and using promoters of Th and Mg and kieselguhr as support. This catalyst was denominated FTStd and has the following texture characteristics determined by nitrogen sorption: specific area (S_{BET}) = 87 m^2 g^{-1}, adsorbed volume (V_{ads} (p/p^0 = 0.98)) = 0.27 cc g^{-1}, mean porous diameter = 126 Å. This catalyst was probed in the reaction showing a selectivity and a product distribution similar to that of Co20Loc, especially at temperatures higher than 240°C, although the conversion is higher taking into account the content of the active phase.

To probe that the porous structure plays an important role in the selectivity of Co20Al, two catalysts were supported over SerBcaNa which was treated similarly (pH, dry, calcination) to that used in the pillaring process, without including the oligocation
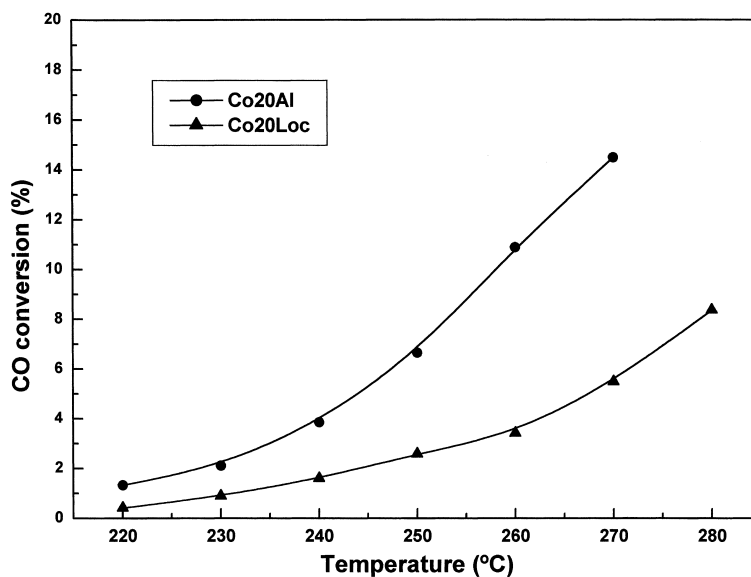

Fig. 5. Catalytic activity in FT synthesis for the Co catalysts supported over Al-PILC.
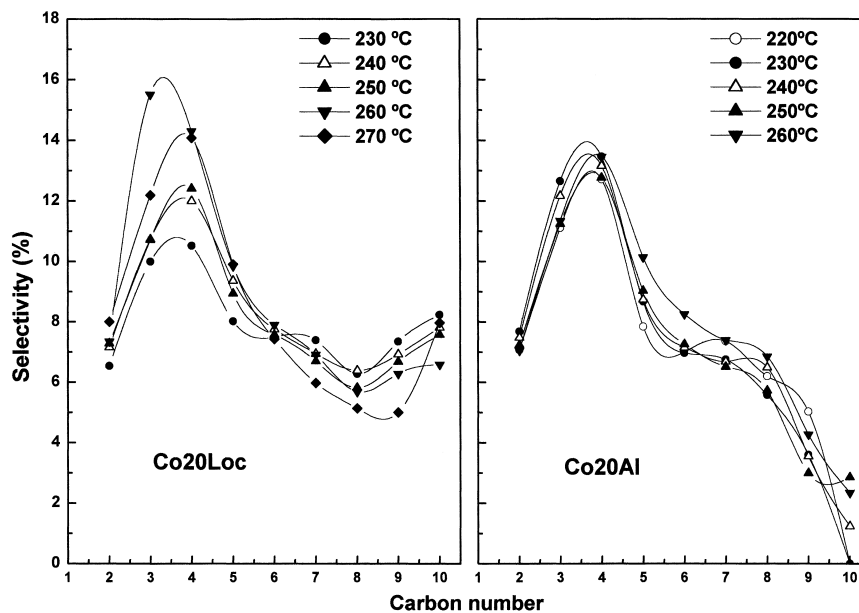
Fig. 6. Distribution of products vs. the chain carbon number, using Co20Al and Co20Loc in FTS at different temperatures.
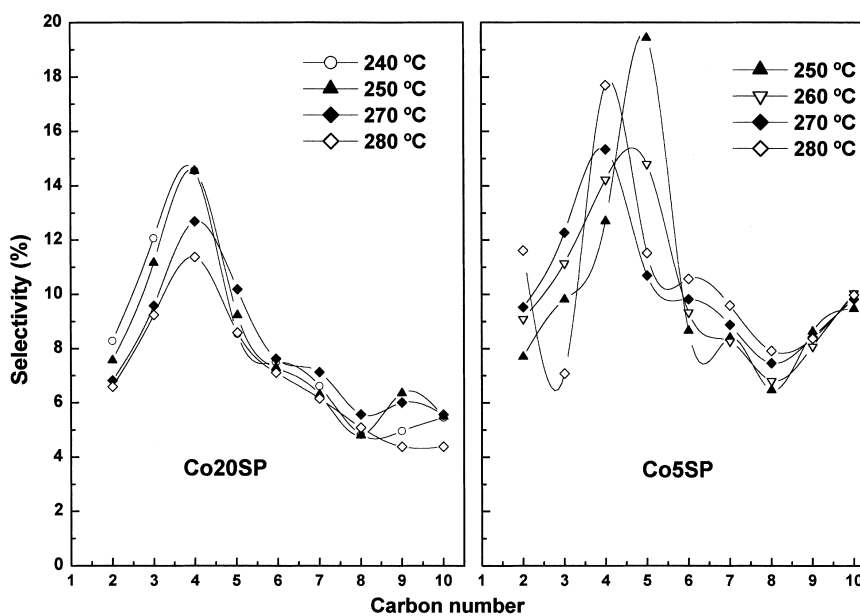

Fig. 7. Distribution of products vs. the chain carbon number for the Co20SP and Co5SP catalysts in FTS at different temperatures.
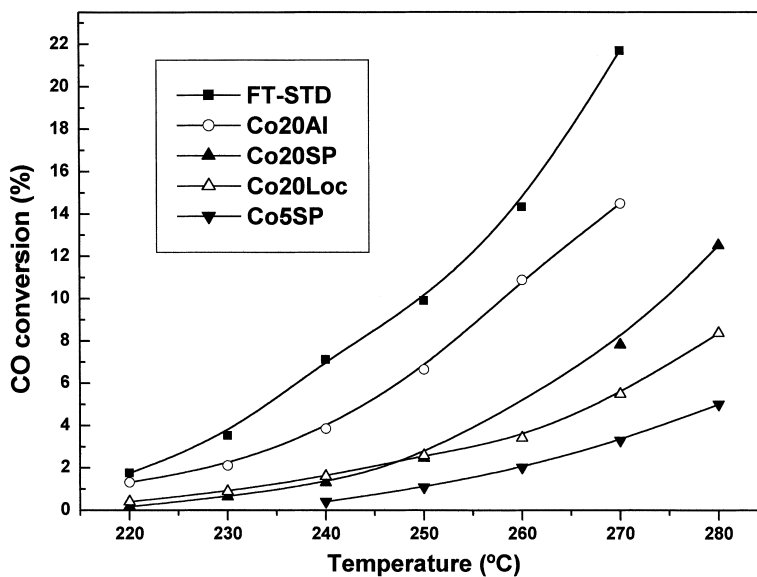
Fig. 8. Comparison of the catalytic activity for all the prepared Co catalysts.

of Al. These catalysts were prepared with two different Co concentrations: one of them with the same content of Co by unit of mass as in Co20Al, which was denominated Co20SP; the other one, having the same surface relationship $Co\,m^{-2}$ as in the Co20Al, and denominated Co5SP. Both catalysts were evaluated in the reaction under the same conditions as described previously. In Fig. 7, it is shown the selectivity versus the number of carbons obtained from Co20SP and Co5SP catalysts. In the distribution of hydrocarbons
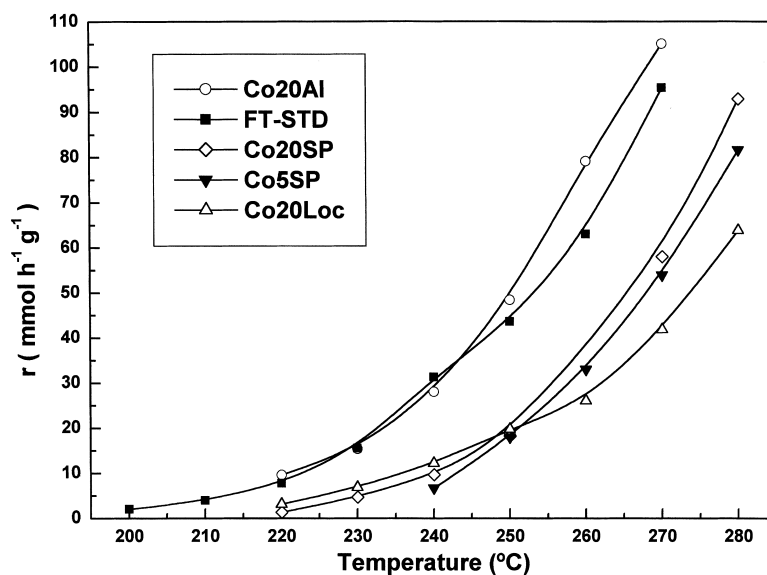

Fig. 9. Intrinsic activity of the prepared Co catalysts in mmols of converted CO per hour and per gram of catalyst vs. temperature.

with Co20SP is not observed the fast diminution of chain carbon growth, resulting much similar to Co20Loc. Due to the low conversion of the Co5SP it is difficult to measure the product distribution. Nevertheless, it follows the trend of the previously described samples.

As a consequence, it can be concluded that it is the pillared support, which produces the diminution in the product distribution for large carbon chains, and not the presence of active phase or its dispersion.

In Fig. 8 the activity of these catalysts is shown. The standard catalyst has a higher conversion than Co20Al, probably due to the higher content of active phase (30% against 20%), being the last one more active than the other ones. The conversion obtained with Co20SP is similar to Co20Loc. For Co5SP there is not conversion under 240°C and is always low.

In Fig. 9 the rate of CO conversion (in mmol of CO per hour) by active phase mass (in g) versus temperature is shown. From this figure, we conclude that the Co20Al catalyst has higher activity by mass unit than the standard catalyst, even in the absence of promoter. Both catalysts have higher activity than the others, being Co20Loc the least active one. The difference between Co20SP and Co5SP are due exclusively to the quantity of Co incorporated.

The analysis of the porosity of the samples supported over Al500 and Loc500 shows that, after the incorporation of the active phase, the porous structure of Co20Al is the least altered, showing porous between 10–50 Å that not occurs with Co20Loc. Then, the selectivity to the hydrocarbon chains of Co20Al is due exclusively to the microtexture and structure of the support.

4. Conclusions

The activity is in relation with the active phase, more than with the dispersion, becoming higher when the content increases.

Loc500 acts as a conventional support without any additional effect of its texture. It is due to the fact that a part of the active phase is over the surface of the solid, generating a structure proper of the oxides, whereas the other is blocking the microporous, and cannot show their action as confined environment.

The catalyst supported over pillared clay by the conventional method, Al500, shows size selectivity. The texture of the support that has been better preserved under the incorporation of the active phase leads the reaction to the formation of liquid hydrocarbons.

The pillared clays are adequate as catalyst supports with interesting characteristics if compared with conventional supports. In the case of FT synthesis, they lead the selectivity of the product, in their best behaviour, or at least act as a conventional support.

To finish, we emphasise that the Co20Al catalyst exceeds highly the proposed aim, because of its activity, with a conversion similar to a standard catalyst and because of its selectivity to liquid hydrocarbons, by effect of the texture of the support compared with the standard FT catalyst.

Additionally, its low selectivity to undesired products as CO_2, which could deactivate the catalyst and the low production of waxes, increases its qualities.

References

[1] K. Sapag, Ph.D. Thesis, Universidad Autónoma de Madrid, Madrid, Spain, 1997.
[2] M.A. Vannice, Cat. Rev. Sci. Eng. 14 (2) (1976) 153–191.
[3] M.E. Dry, The Sasol Fischer–Tropsch processes, in: B. Leach (Ed.), Applied Industrial Catalysis, Academic Press, New York, Vol. 2, 1983 (Chapter 5), p. 167–213.
[4] D.V. Krylow, O.S. Morozova, T.I. Knomenko, Kinet. Catal. 35 (6) (1994) 741–755.
[5] R.B. Anderson, P.H. Emmet (Ed.), Catalysis, Rheinhold, New York, 1956, Vol. 4, p. 257.
[6] H. Pines, The Chemistry of Catalytic Hydrocarbon Conversions, Academic Press, 1981, pp. 276–293.
[7] S.C. Chuang, Y.H. Tian, J.G. Goodwin, I. Wender, J. Catal. 96 (1985) 396–407.
[8] J.E. Lyons, G.W. Parshall, Catal. Today 22 (1994) 313–334.
[9] M.L. Ocelli, J.G. Parulekar, J.W. Higtower, in: Proceedings of the 8th International Congress on Catalysis IV, 1984, p. 725.
[10] R. Burch, Pillared clays, Catal. Today 3 (1988) 2.
[11] ASTM card, 42-1467-JCPDS-ICDD (1997).
[12] ASTM card, 02-1217-JCPDS-ICDD (1997).
[13] ASTM card, 02-0770-JCPDS-ICDD (1997).
[14] P. Arnoldy, J.A. Moulyn, J. Catal. 93 (1985) 38.
[15] D. Schanke, S. Vada, E.Z. Blekkan, A.M. Hilmen, A. Hoff, A. Holmen, J. Catal. 156 (1995) 85–95.
[16] A.M. Hilmen, D. Xhanke, A. Holmen, Catal. Lett. 38 (1996) 143–147.
[17] R.L. Chin, D.M. Hercules, J. Phys. Chem. 86 (1982) 360.
[18] M.E. Dry, Catalysis Science and Technology, in: J.R. Andersson, M. Boudart (Eds.), The Fischer–Tropsch Synthesis, Springer, Berlin, 1981 (Chapter 4).
[19] J.T. Richardson, Principles of Catalyst Development, Plenum Press, New York, 1989.